ELEMENTAL COMPOSITION OF PALM-OIL MILL BOILER FLYASH

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Submitted for publication to:

ASIAN ENVIRONMENT
(Journal of Environmental Science & Technology
for Balanced Development)
P.O. Box 90,
MCC Makati,
Philippines.

date: January, 1987

(13)

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ABSTRACT

A total of 29 elemental concentrations were determined from two separate samples of palm oil flyash collected downstream of a palm oil mill boiler. These include Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Dy, Eu, Fe, Ga, K, La, Lu, Mn, Na, Sb, Sc, Sm, Rb, Th, Ti, U, V, Yb, and Zn. The results showed that potentially volatile elements like As, Ba, Br, Cl, Co, Cr, Cs, Sb, Rb, and Zn were enriched in the stack-ash emission as compared to retained-ash. Gallium, K, and Na were intermediately enriched and Al, Ca, Ce, Eu, Fe, La, Lu, Mn, Sc, Sm, Th, Ti, V and Yb were equally concentrated in both samples.

INTRODUCTION

Particulate emission from a stationary source like a palm-oil mill operation plant can contribute significantly to the amount of anthropogenic origin especially trace elements.

It is estimated that there are more than 200 palm-oil mills present in this country and these give rise to about 400 boilers and 200 incinerators (Azman & Govalupillay 1986). On average 20 tons or more of both fibres and shells are produced per 100 ton fresh-fruit bunches processed and these are usually consumed in the mill as boiler fuel. The situation will certainly create a great burden of flyash particulate emission if it is not properly controlled. Unfortunately, a significant portion of the flyash is in the respirable size range that can contribute the greatest potential hazard for human inhalation (Mohd. Rashid, 1986).

In view of this, a study was conducted to analyze the elemental composition present in the palm-oil flyash samples collected at two different locations downstream of the palm-oil mill boiler. The elements were detected using a Instrumental Neutron Activation Analyzer. (INAA)

EXPERIMENTAL

Sample collection.

The flyash samples were obtained from a mixed fibre and shell fired-fuel palm-oil mill which has the capacity of processing 20 ton of fresh-fruit bunches per hour. The mill is equipped with 2 boilers (each rated to generate 15,000 kg/hr steam, one as standy) and one unit of multicyclones dust collector. Two samples at different locations downstream of the boilers were collected a) flyash retained in the multicyclones measured to be averaging about 2 kg per minute and b) stack flyash collected in the ducting before leaving the stack exit. The retained sample was collected in bulk and dried in an oven for at least 24 hours. The sample was then sieved mechanically for 63 micron particle size and below before the elemental analysis. The stack flyash was collected isokinetically using portable Anderson universal stack sampler (D 1027). Further description of the equipment and methods of sampling are described in detail elsewhere. (Haaland, 1974)

Elemental Analysis.

The elemental analysis was done by the INAA. The samples and standard were neutron irradiated in a Triga MKII reactor (average flux 3 x 10^{12} ncm^{-2} s^{-1} at 500 kw operating power) for two minutes. A decay time of about 20 minutes was required for the determination of Al, Ba, Ca, Cl, Eu, K, Mn, Na, Ti and V. The counting of active samples and standard were repeated after

24 hours decay in order to enable the analysis of As, Na, K, Dy, and Sm. The remaining elements were analyzed after 14 - 21 days decay of activated samples and standards irradiated for 6 hours. The Reference Material of NBS 1632a Coal ash was used as the standard.

The gamma ray spectra of the radioactive species were taken with a Hyperpure-germinium-semiconductor detector system including ND-66 multichannel analyzer (4096 channel). The FWHM of the system was 1.9 KeV for the 1332 KeV γ-ray peak of ^{60}Co. The spectral data were analyzed on ND6680 with the Nuclear Data Peak Search Program which fit the peaks with Gaussian Function (Thomson and Meyers, 1978).

RESULTS

Results of the analysis of 29 elements in both stack and retained palm-oil flyash samples are listed in Table 1 and 2 respectively. A total of twenty analyses were done for the retained samples whereas only six analyses were possible for the stack samples due to insufficient amount of samples collected near the stack exit. As a result, both Ba and Ti were measured with some uncertainties and these are indicated by the 'less than' signs as in Table 2.

Both Dy and U peaks were not seen in the analysis of stack sample. The authors believed that these elements were below the detection limits due to insufficient amount of samples. No further effort was made to quantified this statement at this stage.

DISCUSSION

Table 3 presents the elemental concentration ratio of stack to retained flyash samples. As can be seen from Table 3, several of the elements were found to be much higher concentration in the stack-ash sample. These include As, Ba, Br, Cl, Co, Cr, Cs, Sb, Rb, and Zn. Arsenic is considered to be a toxic element even in trace amounts. Antimony (Sb) has a similar effect as As if heavily exposed. The concentration of Br and Cl were high in several order of magnitudes in the stack-ash fraction. Their presence in the flyash is probably due to the application of herbicides and insecticides in the field which deposited or later absorbed by the plants.

Table 1. Elemental Concentrations in Retained Flyash*

Element	Mean	Std. dev.
Al (%)	1.79	Ø.32
As	17.9	3.25
Ba	79.1	45.2
Br	23.8	6.5Ø
Ca (%)	1.94	Ø.Ø7
Ce	22.7	3.Ø6
Cl (%)	Ø.35	Ø.Ø2
Co	2.Ø3	Ø.68
Cr	34.2	4.53
Cs	2.13	Ø.54
Dy	1.74	Ø.49
Eu (ppb)	244	36
Fe (%)	1.46	Ø.11
Ga	3.64	1.89
K (%)	5.24	Ø.39
La	13.7	1.49
Lu (ppb)	211	18.Ø
Mn	79Ø	61.5
Na (%)	Ø.Ø7	Ø.ØØ4
Sb	Ø.75	Ø.26
Sc	3.Ø2	Ø.22
Sm	1.78	Ø.25
Rb	311	57.3
Th	4.31	Ø.75
Ti (%)	Ø.13	Ø.Ø3
U	1.37	Ø.42
V	22.6	8.Ø8
Yb	Ø.87	Ø.16
Zn	122	18.9

*Concentration in ppm or otherwise stated.

*Table 2. Elemental Concentrations in Stack Flyash**

Element	Mean	Std. dev.
Al (%)	1.44	Ø.27
As	1ØØ	42.5
Ba	<535	
Br	373	45.6
Ca (%)	1.22	Ø.Ø9
Ce	19.7	2.5Ø
Cl (%)	4.78	Ø.98
Co	23.Ø	5.69
Cr	261-	51.6
Cs	5.44	Ø.72
Dy	NS	
Eu (ppb)	1.38	Ø.2Ø
Fe (%)	1.27	Ø.28
Ga	7.26	2.65
K (%)	9.52	1.Ø5
La	8.36	2.16
Lu (ppb)	162	2Ø.Ø
Mn	741	78.4
Na (%)	Ø.Ø9	Ø.Ø1
Sb	2.6Ø	Ø.57
Sc	1.96	Ø.21
Sm	Ø.99	Ø.15
Rb	753	2Ø.5
Th	3.91	1.Ø4
Ti (%)	<Ø.Ø6	
U	NS	
V	4.68	1.3Ø
Yb	Ø.4Ø	Ø.Ø5
Zn	356	49.4

* Concentration in ppm or otherwise stated, NS = not seen.

Table 3. Flyash Elemental Concentration Ratios*

Element	Stack	Retained	Stack/Retained
Al (%)	1.44	1.79	Ø.8
As	1ØØ	17.9	5.6
Ba	<535	79.Ø	6.8
Br	373	23.8	16
Ca (%)	1.22	1.94	Ø.6
Ce	19.7	22.7	Ø.9
Cl (%)	4.78	Ø.35	14
Co	23.Ø	2.Ø3	11
Cr	261	34.2	7.6
Cs	5.44	2.13	2.5
Dy	NS	1.74	-
Eu (ppb)	1.38	244	Ø.Ø1
Fe (%)	1.27	1.46	Ø.9
Ga	7.26	3.64	2.Ø
K (%)	9.52	5.24	1.8
La	8.36	13.7	Ø.6
Lu (ppb)	162	211	Ø.8
Mn	741	79Ø	Ø.9
Na (%)	Ø.Ø9	Ø.Ø7	1.3
Sb	2.6Ø	Ø.75	3.5
Sc	1.96	3.Ø2	Ø.6
Sm	Ø.99	1.78	Ø.6
Rb	753	311	2.4
Th	3.91	4.31	Ø.9
Ti (%)	<Ø.Ø6	Ø.13	Ø.5
U	NS	1.37	-
V	4.68	22.6	Ø.2
Yb	Ø.4Ø	Ø.87	Ø.5
Zn	356	122	2.9

* concentration in ppm or otherwise stated, NS = not seen

The high concentrations of As, Ba, Br, Cl, Co, Cr, Cs, Sb, Rb and Zn in the stack-ash emission could infer that these elements were in the submicron sized particles. It also suggested that these elements had a lower degree of volatilazation temperature and that they could easily evaporate in the combustion zone and condensed on the particles surface. The condensation phenomena may be aggravated during feeding the boiler manually with the solid-fuel (fibres and shells). A tremendous amount of fine flyash would be produced in the combustion chamber during this process. It was also suggested that multicyclones are not efficient for submicron sized particles collection.

The other group of the elements mainly Al, Ca, Ce, Eu, Fe, La, Lu, Mn, Sc, Sm, Th, Ti, V and Yb were found equally concentrated in both of the samples. The elemental stack to retained concentration ratios showed no signs of enrichment for these elements. These elements were well retained in the dust collector and believed to be in the supermicron sized particles. In fact many of these are not easily volatilised even during the combustion processes. Given the fact that there were no data on flyash size available, only rough inferences could be made to date based on these findings.

Gallium, K and Na were intermediately enriched in the stack-ash emission. Their elemental ratios were slightly higher than one but the enrichments were very minimal to allow any other judgement to be made on them.

CONCLUSION

Based on the elemental ratios of stack to retained palm-oil flyash reveal that As, Ba, Br, Cl, Co, Cr, Cs, Sb, Rb and Zn are mainly concentrated in the stack-ash emission. Gallium, K, and Na, are intermediately enriched and Al, Ca, Ce, Eu, Fe, La, Lu, Mn, Sc, Sm, Th, Ti, V and Yb show no significant enrichment in the stack sample. We conclude that certain elements in the palm-oil flyash are more concentrated on the finer-flyash particles that escape the emission control system and are emitted into the atmosphere. The environment is more likely to be exposed to these fine particles because of their longer atmospheric residence times (compared to larger particles). Also, the situation may affect mill workers especially with regard to possible eventual deep lung deposition. Consequently, further studies on this subject especially on size characterization of palm-oil flyash and potentially toxic elements are warranted.

Acknowledgements

The authors wish to thank Harissons Malaysian Plantations Berhad for giving the permission to conduct the study and Ms. Latnah Ninggal for typing this manuscript.

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